SYNTHESIS AND CHARACTERIZATION OF UNDOPED AND DOPED CdS/TiO$_2$ PHOTOANODES

a thesis submitted by
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in partial fulfillment for the award of the degree of
DOCTOR OF PHILOSOPHY

under the Supervision of
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DECLARATION

I, SAINTA JOSTAR. T hereby declare that the thesis, entitled “Synthesis and characterization of undoped and doped CdS/TiO$_2$ photoanodes”, submitted to the Karunya University, in partial fulfillment of the requirements for the award of the Degree of Doctor of Philosophy in Physics is a record of original and independent research work done by me during the period 2011 – 2015, under the Supervision and guidance of Dr. Suganthi Devadason, Professor, Department of Physics, Hindustan University, Chennai and under the Joint Supervision of Dr. J. Suthagar, Professor, Engineering Department, Ibri College of Technology, Sultanate of Oman. The work contained in this thesis has not been previously submitted to meet the requirements for a degree or diploma at this or any other higher education institution.

SAINTA JOSTAR. T
BONAFIDE CERTIFICATE

Certified that this Thesis titled, “Synthesis and characterization of undoped and doped CdS/TiO₂ photoanodes” is the bonafide work of SAINTA JOSTAR. T who carried out the research under my supervision. Certified further, that to the best of my knowledge the work reported herein does not form part of any other thesis or dissertation on the basis of which a degree or award was conferred on an earlier occasion on this or any other scholar.

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ABSTRACT

In the present work, undoped and doped CdS nanocrystals as a sensitizer were grown on the spin coated nanoporous TiO$_2$ film by repeated cycles of successive ionic layer adsorption and reaction (SILAR) method. ZnS layer was coated on the undoped and doped CdS/TiO$_2$ anodes to act as a protective layer on CdS. Thus, the prepared ZnS with undoped and doped CdS/TiO$_2$ films can be used as a photoanode for semiconductor sensitized solar cell.

The prepared undoped (ZnS/CdS/TiO$_2$) and doped (ZnS/Mn-CdS/TiO$_2$, ZnS/Co-CdS/TiO$_2$) photoanodes were characterized by XRD, Raman, SEM with EDX, TEM, PL, UV and I-V analysis. From XRD pattern, it is observed that the undoped CdS film shows the crystallite size of 3 nm. The optical band gap of the undoped film determined from transmittance spectra decreases from 3.46 to 2.15 eV with the increase in the number of CdS SILAR cycles. SEM and TEM analysis of undoped film depict the enabled penetration of CdS (111) nanoparticles into the nanoporous TiO$_2$ (101) structure. EDX study confirms the presence of all the elements (Ti, Cd, S, Zn and O) found on the photoanode. The interlocking of cubic structured CdS on anatase phase of TiO$_2$ in the photoanode is verified using Raman spectra. Photoluminescence (PL) study shows that the emission peak corresponding to TiO$_2$ has been slightly blue shifted due to the
interaction of CdS nanoparticles in TiO$_2$ nanoporous structures. The electrical measurement of the undoped electrode shows that the dark and light illuminated resistivity values of the ZnS/12CdS/TiO$_2$ photoanode are 7.91 and 5.65 $\Omega$.cm, respectively.

Doping is necessary to improve the intrinsic property of semiconducting nanocrystals. Doping optically active transition metal ions like Mn$^{2+}$ and Co$^{2+}$ can change the electronic and photophysical properties of nanocrystal. Moreover, doping the transition metal ion with CdS can induce charge separation and recombination dynamics. Hence, the dopant ion Mn$^{2+}$ or Co$^{2+}$ was introduced with CdS to enhance the optical and electrical properties of the photoanode.

The structure and morphology of Mn-doped semiconductor sensitized photoanodes depict the enabled diffusion of CdS nanoparticles into the nanoporous TiO$_2$ structure. The calculated crystallite size of Mn-doped CdS nanocrystals is found to be 2 nm from XRD pattern. The optical absorption results reveal that Mn-doping with CdS could greatly enhance the absorption of TiO$_2$ in the visible region, leading to a decrease in the bandgap energy from 3.43 to 2.02 eV. PL spectrum displays two strong emission peaks one at near UV (367 nm) and the other at violet region (411 nm) with an additional low intensity red emission peak at 633 nm due to oxygen vacancies and defects. It has been demonstrated that the doping of Mn$^{2+}$ with CdS on the surface of the TiO$_2$ nanostructured film could improve the electrical performance of the anode through rapid electron transport by enhanced absorption of the incident light.
The structure and morphology of Co-doped anodes reveal the formation of Co-doped cubic CdS nanoparticles into the anatase phase of TiO$_2$ film. The electrical characterization studies (I-V) of the doped electrode exhibit that incorporation of Co$^{2+}$ with CdS on the surface of the TiO$_2$ nanoporous film could lower the resistance upon illumination with visible light.
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SAINTA JOSTAR. T
## CONTENTS

<table>
<thead>
<tr>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>DECLARATION</td>
<td>ii</td>
</tr>
<tr>
<td>BONAFIDE CERTIFICATE</td>
<td>iii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>iv</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENT</td>
<td>vii</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>viii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xvi</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>xvii</td>
</tr>
<tr>
<td>LIST OF SYMBOLS AND ABBREVIATIONS</td>
<td>xxii</td>
</tr>
<tr>
<td>1. INTRODUCTION, BACKGROUND THEORY AND</td>
<td>1</td>
</tr>
<tr>
<td>LITERATURE REVIEW</td>
<td></td>
</tr>
<tr>
<td>1.1 Introduction</td>
<td>1</td>
</tr>
<tr>
<td>1.2 Overview of solar cells</td>
<td>2</td>
</tr>
<tr>
<td>1.3 Significance of photoanode for SSSCs</td>
<td>4</td>
</tr>
<tr>
<td>1.3.1 Importance of TiO₂</td>
<td>5</td>
</tr>
<tr>
<td>1.3.2 Importance of CdS as sensitizer</td>
<td>7</td>
</tr>
<tr>
<td>1.3.3 Importance of ZnS</td>
<td>8</td>
</tr>
</tbody>
</table>
1.4 Background theory of the materials

1.4.1 Overview of TiO$_2$

1.4.1.1 Structure and properties of TiO$_2$  
1.4.1.2 Applications of TiO$_2$  

1.4.2 Discovery of CdS  

1.4.2.1 Structure and properties of CdS  

1.4.2.2 Application of CdS  

1.4.3 Discovery of ZnS  

1.4.3.1 Structure and properties of ZnS  

1.4.3.2 Applications of ZnS  

1.5 Literature review  

1.5.1 Review on the preparation methods of bare TiO$_2$, undoped and doped CdS sensitized TiO$_2$ film  

1.5.2 Review on the structural studies of bare TiO$_2$, undoped and doped CdS sensitized TiO$_2$ thin films  

1.5.3 Review on the optical properties of bare TiO$_2$, undoped and doped CdS sensitized TiO$_2$ thin films  

1.5.4 Review on the surface morphology of bare TiO$_2$, undoped and doped CdS sensitized TiO$_2$ thin films  

1.5.5 Review on the electrical properties of bare TiO$_2$, undoped and doped CdS sensitized TiO$_2$ thin films  

1.6 Objective of the work
2. EXPERIMENTAL AND CHARACTERIZATION TECHNIQUES OF PHOTOANODE

2.1 Introduction

2.2 Chemical method

   2.2.1 Spin coating technique

   2.2.2 Successive Ionic Layer Absorption and Reaction (SILAR) method

2.3 Experimental technique

   2.3.1 Materials

   2.3.2 Substrate cleaning procedure

   2.3.3 Synthesis of ZnS/undoped CdS sensitized nanoporous TiO$_2$ (ZnS/CdS/TiO$_2$) films

   2.3.4 Synthesis of ZnS/doped CdS sensitized nanoporous TiO$_2$ (ZnS/doped CdS/TiO$_2$) films

2.4 Characterization techniques

   2.4.1 X-ray diffraction (XRD)

      2.4.1.1 Bragg’s law

      2.4.1.2 Evaluation of structural parameters

      2.4.1.3 Instrumentation

   2.4.2 Raman spectroscopy
2.4.2.1 Principle
2.4.2.2 Components of Raman spectrometer
2.4.2.3 Instrumentation
2.4.3 UV-visible spectroscopy (UV-Vis)
  2.4.3.1 Principle
  2.4.3.2 Components of UV-visible spectrophotometer
  2.4.3.3 Instrumentation
2.4.4 Photoluminescence spectroscopy (PL)
  2.4.4.1 Principle
  2.4.4.2 Components of photoluminescence spectrophotometer
  2.4.4.3 Instrumentation
2.4.5 Scanning electron microscope (SEM)
  2.4.5.1 Principle
  2.4.5.2 Components of scanning electron microscope
  2.4.5.3 Instrumentation
2.4.6 Energy dispersive X-ray spectroscopy (EDX)
2.4.7 Transmission electron microscope (TEM)
  2.4.7.1 Principle
  2.4.7.2 Components of transmission electron microscopy
  2.4.7.3 Instrumentation
2.4.8 Current-voltage (I-V) measurement

2.4.8.1 Principle

2.4.8.2 Instrumentation

2.5 Conclusion

3. EFFECT OF CdS LAYERS ON THE STRUCTURAL AND OPTICAL PROPERTIES OF ZnS/CdS/TiO₂ PHOTOANODES

3.1 Introduction

3.2 Experimental method for synthesis of undoped (ZnS/CdS/TiO₂) photoanodes

3.2.1 Synthesis of nanoporous TiO₂ films

3.2.2 Deposition of CdS on nanoporous TiO₂ films

3.2.3 Deposition of ZnS coating on CdS/TiO₂ films

3.3 Characterization

3.4 Results and discussion

3.4.1 Structural analysis

3.4.1.1 X-ray diffraction

3.4.1.2 Raman spectroscopy

3.4.2 Morphology and elemental composition analysis

3.4.2.1 Surface electron microscopy

3.4.2.2 Transmission electron microscopy

3.4.3 Optical analysis
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.4.3.1 UV-vis spectroscopy</td>
<td>82</td>
</tr>
<tr>
<td>3.4.3.2 Photoluminescence spectroscopy</td>
<td>86</td>
</tr>
<tr>
<td>3.4.4 Electrical studies: I-V characterization</td>
<td>88</td>
</tr>
<tr>
<td>3.5 Conclusions</td>
<td>89</td>
</tr>
<tr>
<td><strong>4. INFLUENCE OF Mn-DOPING WITH CdS ON THE STRUCTURAL AND OPTICAL PROPERTIES OF ZnS/CdS/TiO₂ PHOTOANODES</strong></td>
<td>91</td>
</tr>
<tr>
<td>4.1 Introduction</td>
<td>91</td>
</tr>
<tr>
<td>4.2 Experimental method for synthesis of doped (ZnS/Mn-CdS/TiO₂) photoanodes</td>
<td>92</td>
</tr>
<tr>
<td>4.2.1 Synthesis of Mn-doped CdS sensitizer in ZnS/CdS/TiO₂ photoanodes</td>
<td>92</td>
</tr>
<tr>
<td>4.3 Characterization</td>
<td>93</td>
</tr>
<tr>
<td>4.4 Results and discussion</td>
<td>93</td>
</tr>
<tr>
<td>4.4.1 Structural analysis</td>
<td>93</td>
</tr>
<tr>
<td>4.4.1.1 X-ray diffraction</td>
<td>94</td>
</tr>
<tr>
<td>4.4.1.2 Raman spectroscopy</td>
<td>96</td>
</tr>
<tr>
<td>4.4.2 Morphology and elemental composition analysis</td>
<td>97</td>
</tr>
<tr>
<td>4.4.2.1 Surface electron microscopy</td>
<td>97</td>
</tr>
<tr>
<td>4.4.2.2 Transmission electron microscopy</td>
<td>99</td>
</tr>
<tr>
<td>4.4.3 Optical analysis</td>
<td>100</td>
</tr>
</tbody>
</table>
4.4.3.1 UV-vis spectroscopy
4.4.3.2 Photoluminescence spectroscopy
4.4.4 Electrical studies
4.5 Conclusions

5. IMPROVED STRUCTURAL AND OPTO-ELECTRONIC PROPERTIES OF Co-DOPED CdS ON ZnS/CdS/TiO_2 PHOTOANODES

5.1 Introduction
5.2 Experimental method for synthesis of doped (ZnS/Co-CdS/TiO_2) photoanodes
  5.2.1 Synthesis of Co-doped CdS sensitization on ZnS/CdS/TiO_2 photoanode
5.3 Characterization
5.4 Results and discussion
  5.4.1 Structural analysis
    5.4.1.1 X-ray diffraction
    5.4.1.2 Raman spectroscopy
  5.4.2 Morphological analysis
    5.4.2.1 Surface electron microscopy
    5.4.2.2 Transmission electron microscopy
  5.4.3 Optical analysis
5.4.3.1 UV-vis spectroscopy 117
5.4.3.2 Photoluminescence spectroscopy 119
5.4.4 Electrical Studies 120
5.5 Conclusions 122

6. SYNTHESIS OF RESULTS FOR UNDOPED AND DOPED FILMS 124

6.1 Introduction 124
6.2 Structural studies 124
6.3 Optical studies 126
6.4 Electrical studies 128
6.5 Conclusions 130

7. CONCLUSIONS AND FUTURE OUTLOOK 131

7.1 Conclusions 131
7.2 Future outlook 132

REFERENCES 134

LIST OF PUBLICATIONS 142
CURRICULUM VITAE 144
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table. No</th>
<th>Table captions</th>
<th>Page. No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Table 1.1</td>
<td>Discovery and development of TiO$_2$ for potential applications</td>
<td>9</td>
</tr>
<tr>
<td>Table 1.2</td>
<td>Standard properties of TiO$_2$</td>
<td>12</td>
</tr>
<tr>
<td>Table 1.3</td>
<td>Physical properties of TiO$_2$</td>
<td>13</td>
</tr>
<tr>
<td>Table 1.4</td>
<td>General properties of CdS</td>
<td>16</td>
</tr>
<tr>
<td>Table 1.5</td>
<td>General properties of ZnS</td>
<td>19</td>
</tr>
<tr>
<td>Table 3.1</td>
<td>Structural parameters of porous TiO$_2$ and ZnS/12CdS/TiO$_2$ thin film</td>
<td>75</td>
</tr>
<tr>
<td>Table 4.1</td>
<td>Structural parameters of the undoped and Mn-doped photoanode obtained from the XRD profiles</td>
<td>95</td>
</tr>
<tr>
<td>Table 5.1</td>
<td>Structural parameters of the undoped and Co-doped photoanode obtained from the XRD profiles</td>
<td>112</td>
</tr>
<tr>
<td>Table 6.1</td>
<td>PL emission peak intensity of undoped and doped films</td>
<td>127</td>
</tr>
<tr>
<td>Table 6.2</td>
<td>Resistivity of undoped and doped films</td>
<td>129</td>
</tr>
</tbody>
</table>
### LIST OF FIGURES

<table>
<thead>
<tr>
<th>Fig. No</th>
<th>Figure caption</th>
<th>Page. No</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fig. 1.1</td>
<td>Structure of TiO$_2$ (a) anatase (b) rutile and (c) brookite</td>
<td>11</td>
</tr>
<tr>
<td>Fig. 1.2</td>
<td>Elementary cell of TiO$_2$ polymorphs</td>
<td>14</td>
</tr>
<tr>
<td>Fig. 1.3</td>
<td>Structure of CdS (a) hexagonal and (b) zinc blende</td>
<td>16</td>
</tr>
<tr>
<td>Fig. 1.4</td>
<td>Schematic representation of unit cells for ZnS phases (a) zinc blende (b) wurtzite and (c) rock salt</td>
<td>18</td>
</tr>
<tr>
<td>Fig. 1.5</td>
<td>XRD patterns of as-prepared TiO$_2$ nanocrystals (a) T-120, (b) T-140 (c) T-160 (d) T-180 and (e) D-140</td>
<td>26</td>
</tr>
<tr>
<td>Fig. 1.6</td>
<td>Raman spectra of TiO$_2$ films coated with CdS for various number (n= 3, 5, 7 and 11) of SILAR cycles</td>
<td>27</td>
</tr>
<tr>
<td>Fig. 1.7</td>
<td>Absorption spectra of TiO$_2$ nanorods covered with CdS deposited for 0, 2, 3, 4 and 5h</td>
<td>31</td>
</tr>
<tr>
<td>Fig. 1.8</td>
<td>HR-TEM images of the CdS(6)/TiO$_2$ film</td>
<td>33</td>
</tr>
<tr>
<td>Fig. 2.1</td>
<td>Spin coater (HOLMARC)</td>
<td>38</td>
</tr>
<tr>
<td>Fig. 2.2</td>
<td>The schematics of spin coating</td>
<td>39</td>
</tr>
<tr>
<td>Fig. 2.3</td>
<td>Bragg’s diffraction condition</td>
<td>44</td>
</tr>
<tr>
<td>Fig. 2.4</td>
<td>Shimadzu XRD-6000 diffractometer</td>
<td>46</td>
</tr>
<tr>
<td>Fig. 2.5</td>
<td>Micro Raman spectrometer (LabRAM HR)</td>
<td>50</td>
</tr>
<tr>
<td>Fig. 2.6</td>
<td>Schematic of UV-visible spectrophotometer</td>
<td>53</td>
</tr>
<tr>
<td>Fig. 2.7</td>
<td>JASCO-UV–VIS–NIR spectrophotometer (JASCO V630)</td>
<td>54</td>
</tr>
<tr>
<td>Fig. 2.8</td>
<td>Block diagram of photoluminescence spectrophotometer</td>
<td></td>
</tr>
<tr>
<td>Fig. 2.9</td>
<td>Jasco FP- 8200 spectrofluorimeter</td>
<td></td>
</tr>
<tr>
<td>Fig. 2.10</td>
<td>Schematic representation of scanning electron microscope</td>
<td></td>
</tr>
<tr>
<td>Fig. 2.11</td>
<td>High resolution scanning electron microscope (FEI Quanta FEG 200)</td>
<td></td>
</tr>
<tr>
<td>Fig. 2.12</td>
<td>X-rays emitted as electrons transfer from a higher energy shell to a lower energy</td>
<td></td>
</tr>
<tr>
<td>Fig. 2.13</td>
<td>Schematic view of transmission electron microscope</td>
<td></td>
</tr>
<tr>
<td>Fig. 2.14</td>
<td>Transmission electron microscope (TEM, JEOL 2100)</td>
<td></td>
</tr>
<tr>
<td>Fig. 2.15</td>
<td>PXI-1044 National instrument workstation</td>
<td></td>
</tr>
<tr>
<td>Fig. 3.1</td>
<td>Schematic process of growth of CdS sensitizer loaded TiO$_2$ film by chemical bath deposition (CBD)</td>
<td></td>
</tr>
<tr>
<td>Fig. 3.2</td>
<td>XRD patterns of (a) porous TiO$_2$ and (b) ZnS/12CdS/TiO$_2$ thin film</td>
<td></td>
</tr>
<tr>
<td>Fig. 3.3</td>
<td>Raman scattering patterns of (a) TiO$_2$ and (b) ZnS/12CdS/TiO$_2$ photoanode</td>
<td></td>
</tr>
<tr>
<td>Fig. 3.4</td>
<td>(a, b) Top surface (c) cross-sectional SEM images (d) the elemental composition of the bare nanoporous TiO$_2$ film</td>
<td></td>
</tr>
<tr>
<td>Fig. 3.5</td>
<td>(a, b) Top surface (c) cross-sectional SEM images (d) the elemental composition of the ZnS/12CdS/TiO$_2$ photoelectrode</td>
<td></td>
</tr>
<tr>
<td>Fig. 3.6</td>
<td>TEM images of (a) low resolution, (b) lattice spacing (c) selected area electron diffraction (SAED) pattern and (d) EDS spectrum of the ZnS/12CdS/TiO$_2$ photoanode</td>
<td></td>
</tr>
<tr>
<td>Fig. 3.7</td>
<td>(a) Absorbance (b) transmittance and (c) band gap of</td>
<td></td>
</tr>
</tbody>
</table>
spin coated nanoporous TiO$_2$ film

Fig. 3.8 Absorption spectra of ZnS/yCdS/TiO$_2$ electrodes 84
Fig. 3.9 Transmittance spectra of ZnS/yCdS/TiO$_2$ electrodes 85
Fig. 3.10 Band gap of ZnS/yCdS/TiO$_2$ electrodes for (a) y= 4
(b) y= 8 and (c) y= 12 85
Fig. 3.11 Photoluminescence spectra of TiO$_2$ and ZnS/12CdS/TiO$_2$ electrodes 87
Fig. 3.12 Proposed energy band structure of ZnS/CdS/TiO$_2$ electrode 88
Fig. 3.13 Dark and light illuminated I-V measurement of ZnS/12CdS/TiO$_2$ electrode coated on glass substrate 89
Fig. 4.1 XRD pattern of (a) ZnS/12CdS/TiO$_2$ and (b) ZnS/10Mn-CdS/TiO$_2$ thin films 95
Fig. 4.2 Raman scattering spectra of (a) ZnS/12CdS/TiO$_2$ and (b) ZnS/10Mn-CdS/TiO$_2$ photoanodes 97
Fig. 4.3 (a, b) Top (c) side-view SEM images and (d) elemental composition of the ZnS/10Mn-CdS/TiO$_2$ photoelectrode 98
Fig. 4.4 TEM images of (a) low resolution (b) high resolution showing lattice spacing (c) selected area electron diffraction (SAED) pattern and (d) EDS spectrum of the ZnS/10Mn-CdS/TiO$_2$ photoanode 100
Fig. 4.5 Absorption spectra of ZnS/yMn-CdS/TiO$_2$ electrodes 101
Fig. 4.6 Transmittance spectra of ZnS/yMn-CdS/TiO$_2$ electrodes 102
Fig. 4.7 Band gap of ZnS/12CdS/TiO$_2$ electrode 102
Fig. 4.8 Band gap of ZnS/10Mn-CdS/TiO$_2$ electrode 103
Fig. 4.9 PL spectra of (a) ZnS/12CdS/TiO$_2$ and (b) ZnS/10Mn-CdS/TiO$_2$ electrodes 104
Fig. 4.10  TiO$_2$/CdS energy level structure diagram of undoped and Mn-doped electrodes

Fig. 4.11  Dark and light illuminated I-V measurement of ZnS/12CdS/TiO$_2$ and ZnS/10Mn-CdS/TiO$_2$ electrodes

Fig. 5.1  XRD pattern of (a) ZnS/12CdS/TiO$_2$ and (b) ZnS/10Co-CdS/TiO$_2$ thin films

Fig. 5.2  Raman scattering spectra of (a) ZnS/12CdS/TiO$_2$ and (b) ZnS/10Co-CdS/TiO$_2$ photoanodes

Fig. 5.3  (a, b) Top (c) side-view SEM images and (d) elemental composition of the ZnS/10Co-CdS/TiO$_2$ photoelectrode

Fig. 5.4  TEM images of (a) low resolution (b) high resolution showing lattice spacing (c) selected area electron diffraction (SAED) pattern and (d) EDS spectrum of the ZnS/10Co-CdS/TiO$_2$ photoanode

Fig. 5.5  Absorption spectra of ZnS/yCo-CdS/TiO$_2$ electrodes

Fig. 5.6  Band gap of ZnS/yCo-CdS/TiO$_2$ electrodes

Fig. 5.7  PL spectra of (a) ZnS/12CdS/TiO$_2$ and (b) ZnS/10Co-CdS/TiO$_2$ electrodes

Fig. 5.8  TiO$_2$/CdS energy level structure diagram of undoped and Co-doped electrodes

Fig. 5.9  Dark and light illuminated I-V measurement of ZnS/12CdS/TiO$_2$ and ZnS/10Co-CdS/TiO$_2$ electrodes

Fig. 6.1  Bar chart of crystallite size for undoped and doped (Mn, Co) films

Fig. 6.2  Comparison of strain in undoped and doped (Mn, Co) films

Fig. 6.3  Comparison of band gap for undoped and doped (Mn, Co) films
Fig. 6.4  PL spectra of undoped and doped (Mn, Co) films  128

Fig. 6.5  Light illuminated I-V measurement of undoped and doped (Mn, Co) films  129
## LIST OF SYMBOLS AND ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>BSE</td>
<td>Backscattered electrons</td>
</tr>
<tr>
<td>CBD</td>
<td>Chemical bath deposition</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge coupled devices</td>
</tr>
<tr>
<td>CdS</td>
<td>Cadmium sulfide</td>
</tr>
<tr>
<td>DSSCs</td>
<td>Dye sensitized solar cells</td>
</tr>
<tr>
<td>DT</td>
<td>Dipole treatment</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>HR</td>
<td>High resolution</td>
</tr>
<tr>
<td>HR-TEM</td>
<td>High-resolution transmission electron microscopy</td>
</tr>
<tr>
<td>IPCE</td>
<td>Incident photon to current efficiency</td>
</tr>
<tr>
<td>I-V</td>
<td>Current-voltage</td>
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<tr>
<td>J&lt;sub&gt;sc&lt;/sub&gt;</td>
<td>Short circuit current density</td>
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<tr>
<td>LO</td>
<td>Longitudinal optical</td>
</tr>
<tr>
<td>MEG</td>
<td>Multiple exciton generation</td>
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<tr>
<td>MOSFETs</td>
<td>Metal oxide semiconductor field effect transistors</td>
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<td>NHE</td>
<td>Normal hydrogen electrode</td>
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<tr>
<td>NIR</td>
<td>Near-infrared</td>
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<tr>
<td>PCE</td>
<td>Power conversion efficiency</td>
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<td>PDA</td>
<td>Photodiode arrays</td>
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<td>PEG</td>
<td>Polyethylene glycol</td>
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<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>PL</td>
<td>Photoluminescence</td>
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<td>PMT</td>
<td>Photomultiplier tube</td>
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<td>PV</td>
<td>Photovoltaic</td>
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<td>RS</td>
<td>Rock salt</td>
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<td>SAED</td>
<td>Selected area electron diffraction</td>
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<td>SEM</td>
<td>Scanning electron microscopy</td>
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<td>SEs</td>
<td>Secondary electrons</td>
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<td>SILAR</td>
<td>Successive ionic layer absorption and reaction</td>
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<td>SO</td>
<td>Surface optical</td>
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<td>SPD</td>
<td>Spray pyrolysis deposition</td>
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<td>SSSCs</td>
<td>Semiconductor sensitized solar cells</td>
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<td>TiO$_2$</td>
<td>Titanium dioxide</td>
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<td>TTIE</td>
<td>Titanium(IV) ethoxide</td>
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<td>TTIP</td>
<td>Titanium(IV) isopropoxide</td>
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<td>Wurtzite</td>
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<td>XRD</td>
<td>X-ray diffraction</td>
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<td>ZB</td>
<td>Zinc blende</td>
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